EUROPEAN PATENT APPLICATION

㉗ Applicant: International Business Machines Corporation, Armonk, N.Y. 10504 (US)

㉘ Inventor: Tu, King Ning, 44 Whitlaw Close, Chappaqua New York 10514 (US)
Inventor: Ahn, Kie Yeung, 639 Quaker Road, Chappaqua New York 10514 (US)
Inventor: Herd, Sigrid Renee. South Quakerhill Road, Pawling New York 12564 (US)
Inventor: Lee, Michael Heino. 715 Seawood Way, San Jose California 95120 (US)
Inventor: Wieder, Harold. 20175 Knollwood Drive, Saratogo California 95070 (US)
Inventor: Onton, Aare, 14690 Aloha Avenue, Saratogo California 95070 (US)

㉔ Representative: Chaudhry, Mohammad Saeed, IBM United Kingdom Patent Operations Hursley Park, Winchester Hants, S021 2JN (GB)

�54 Optical storage medium and method of recording data thereon.

㊼ An optical recording medium includes a substrate (S3) carrying first and second adjacent thin layers (A, B) or different materials, which, upon marking with an energy beam, form a marked area having optical properties different from the optical properties of the unmarked area. The optical properties of the marked area has contrast sufficiently different from the optical properties of the unmarked area so that the marked area can be reliably sensed. The first thin layer comprises a metal and the second thin layer comprises a metal or a semiconductor selected from the group comprising germanium or silicon.
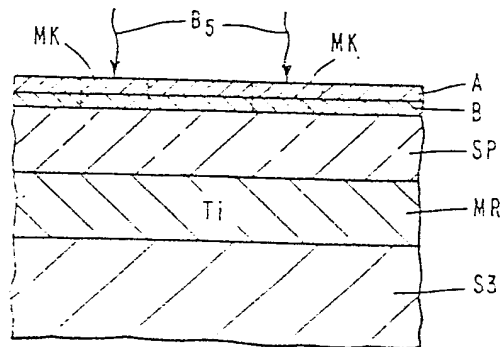
OPTICAL STORAGE MEDIUM AND METHOD OF

RECORDING DATA THEREON

This invention relates to optical storage media and methods of recording thereon.

In optical storage of data, use of lasers to record data optically has been employed in forming pits in a recording medium to change the reflectivity of the medium. Pits are formed by evaporation, melting, or ablation. Recording can be employed which uses changes of reflectivity or transmission of light to indicate data. Bell and Spong in "Anti-reflection Structures for Optical Recording" IEEE Journal of Quantum Electronics QE14, No. 7, 487495 (July 1978) describes on page 489 a monolayer structure of bismuth, titanium, or rhodium. A bi-layer anti-reflection structure can include Al or a dielectric stack of $TiO_2/MgF_2/TiO_2$. Organic dyes such as fluorescein have been used in such recording media. Another structure mentioned on page 493 of Bell and Spong is an Al reflector covered with a dielectric spacer and a Ti absorbing layer. Numerous optical recording variations have been proposed but they will not all be discussed here. The problem with the above alternatives is that they will not provide long-life storage of information without employing strong laser beams.

US 3,959,799 teaches read-only storage media consisting of adjacent thin layers of two or more materials which react, upon heating, to form a reaction product different from those of the reactants. More specifically, a storage medium is described which comprises alternate aluminium and selenium layers which react to form a transparent product, Al_2Se_3, by locally heating the layers such as by the employment of a laser pulse.

U.S. patent 4,069,487 suggests that a laser optical storage system can be used in which a metallic element (selected from Pt, Rh, Au, Ag, Pd, Ir, Cr, Mo, Ta, Zn, Cu, Al, In, Sn, Pb, and Bi Col. 8) can be layered with a non-metallic layer such as a chalcogen compound, inorganic oxide

or resin (dye or pigment). The chalcogens include a chalcogen element such as S, Se and Te.

Widely publicised optical storage materials such as Te and Te-based alloys suffer from relatively short lifetimes primarily because of corrosion of these very thin films on the order of 100 atomic layers. An archival storage system is required to provide data integrity for a period of at least 10 years in an ordinary environment.

U.S. 4,000,492 shows thin metal films upon a transparent substrate with a first layer of Bi, In or Sn and a second layer closer to the laser source composed of BiS_3, SbS_3 and Se.

There have been known in the art optical recording media which result in the removal of material in regions approximating the diffraction-limited spot size of the recording laser. While high contrast between the written and unwritten areas has generally been achieved, the signal-to-noise ratio has been limited in some cases by edge effects around the periphery of the spots, which cause some scattering of the read beam. Additionally, these media, such as those based on Te and Te alloys, suffer from corrosion effects.

There have also been known a number of other optical recording media and other means of marking these media; however, the ones of these media which have achieved long-life recording of information have required higher laser power levels than is desirable, i.e., higher than that achieved with Te-based alloys.

An object of this invention is to provide an optical storage medium which provides extremely high densities of machine readable data.

Another object of this invention is to provide archival level storage of data with assurance of both clarity of the data and long-term retention of the data.

Another object of this invention is to provide an optical recording medium which is capable of storing information in response to a laser beam of acceptable power level and which will also have sufficient lifetime for archival storage purposes.

According to this invention there is provided an optical storage medium including first and second adjacent layers of different materials which, upon marking with an energy beam, form a marked area having optical properties different from the optical properties of the unmarked areas, said first layer comprising a metal; and said second layer comprising a metal or a semiconductor.

Preferably the semiconductor of the second layer is silicon, and the metal of the first layer is a transition metal.

The metals preferred of the first layer include the group VB, VIB, VIIB and VIII elements on the periodic chart, plus Mg and Au. The more advantageous metals include V, Nb, Ta, Cr, Mo, W, Mn, Fe, Co, Rh, Ni, Pd, Pt and Au. Those metals which are most effective include Pd, Pt, Cr, Ta, Rh, V and Co.

The layer in contact with the silicon layer is preferably of a material which can be locally combined or reacted with silicon by local heating to produce a silicide which is an optically distinguishable mark and which is stable.

The silicon layer may be the outer layer so that the other layer is not exposed by prolonged storage in standard ranges of ambient environmental conditions such as those found in offices and conventional manufacturing environments.

The materials of the first and second layers can endothermically combine or react together to form the optically distinguishable marked area. The metals are selected from the group comprising Al, Au, Pb, and Sn and the semiconductors are chosen from the group comprising Ge and Si. The

endothermically formed marked area comprises an alloy or mixture of the materials.

The materials disclosed here produce an optical recording medium capable of recording information at high recording density with acceptable laser power levels and which has lifetime characteristics suitable for archival storage purposes.

According to another aspect of the invention, there is provided a method of recording data for subsequent optical readout, in which an energy beam is used to apply local heating to first and second adjacent layers, one of which layers is of metal and the other of which layers is of metal or semiconductor which can be locally combined or reacted with the metal of the first layer by local heating, to produce an optically distinguishable mark and which is stable.

The relatively short lifetime associated with the conventional Te-based alloys due to corrosion is increased to at least 10 years by use of the materials disclosed herein.

The scope of the invention is defined by the appended claims; and how it can be carried into effect is hereinafter particularly described with reference to the accompanying drawings, in which :-

FIGURE 1 is a schematic drawing of one embodiment of optical storage medium in accordance with this invention;

FIGURE 2 is a similar drawing of another embodiment;

FIGURE 3 is a sectional schematic drawing of a multilayer optical storage medium according to this invention;

FIGURES 4 and 5 show differences in reflectivity between Pd and Pd_2Si and a black reference;

FIGURE 6 is a schematic drawing of an arrangement by which reflectivity was measured;

FIGURE 7 shows percentage of reflectivity versus wavelength for two bi-layers in accordance with this invention;

FIGURE 8 shows glancing-incidence Seeman-Bohlin x-ray diffraction spectra of an Rh/Si film as a function of annealing time;

FIGURE 9 shows percentage of reflectivity versus wavelength for Rh/Si bi-layers;

FIGURE 10 shows reflectivity versus wavelength for Rh/Si before and after annealing;

FIGURE 11 shows percentage of reflectivity versus wavelength for Rh/Si bi-layers;

FIGURE 12 shows percent of reflectivity versus silicon thickness for an Rh/Si bi-layer;

FIGURE 13 is a TEM bright field photograph of a mark written by a laser on a Co/Si bi-layer;

FIGURE 14 is a photograph in the dark field mode of the same mark as in FIG. 13;

FIGURES 15 to 17 show TEM photographs of marks on Au/Si bi-layers of varying compositions;

FIGURE 18 shows reflectivity versus wavelength for a Si/Au bi-layer;

FIGURE 19 shows reflectivity versus wavelength curves for various Si/Pd bi-layers;

FIGURE 20 shows reflectivity percentage versus laser power for Te and Rh/Si bi-layers;

FIGURE 21 shows power versus pulse width as a function for various substrates carrying Te or Rh/Si bi-layers.

FIGURE 22 is a side view of another embodiment of an optical recording medium in accordance with this invention;

FIGURE 23 is a side view of an alternate embodiment of the optical recording medium in accordance with this invention;

FIGURE 24 is a side view of a further embodiment of the optical recording medium in accordance with this invention;

FIGURE 25 is a side view partially in section showing the recording of a marked area in accordance with this invention;

FIGURE 26 is a side view partially in section showing the recorded marked area of the recording medium in accordance with this invention; and

FIGURE 27 is a plan view of the recording medium showing the recorded marked area of FIG. 5.

Figure 1 is a schematic representation of an optical storage medium
according to one embodiment of the invention. The medium comprises
substrate S1 which can be transparent or opaque, depending upon the
application for which the medium is to be employed. Upon the substrate
is a layer in the form of a thin film of silicon (Si). Upon the silicon
layer is another layer in the form of a thin film of a metal M1 which
when heated sufficiently (by means such as laser beam B1) can combine
with the silicon to provide a mark readable by a sensor, such as an
optical sensor of the type employed in optical recording devices. The
data recorded can be stored with such high density that visual inspection
is possible only with optical magnification. In general, the metal
film M1 upon the top of the silicon provides high reflectivity of light.
About 65% and more of beam B1 is reflected. In general, high writing
energy is required to heat the metal M1 sufficiently to form a mark
because of the high level of reflectivity. In addition, the metal film
M1 is exposed to ambient conditions which will tend to shorten the life
of the medium because of oxidation due to humidity causing oxygen to
react with the metal. Such oxidation will spoil the reflectivity of
the metal thereby destroying the contrast in reflectivity required
for storing data. However, if the substrate S1 is transparent, then
the silicon can be exposed to the energy from a source, such as a
laser beam B2, which strikes the silicon which has a low value of
reflectivity less than or equal to about 5%. This leads to a low

7

writing energy because little heating is required to ra' .e the silicon to a high enough temperature to heat the interface between the metal M1 and the silicon to the temperature required to form a mark. In addition, in the case of exposure of the medium through the substrate, the metal M1 can be covered with a protective layer to inhibit degradation of the metal film.

The preferred metals M1 for use in the metal layer are rhodium, cobalt, palladium, platinum, chromium, tantalum and vanadium. In general, the group VB metals V, Nb and Ta are all useful in this connection. Group VIB, VIIB, VIII metals, Mg and Au are all applicable in particular among all other metals. Specifically, the group VIB metals are Cr, Mo, and W. The group VIIB metals are Mn, Tc, and Re. The group VIII metals are Fe, Co, Ni, Ru, Rh, Pd, Os, Ir and Pt. Au is, of course, the nearest neighbour of Pt on the periodic chart although it is a group IB metal.

Another embodiment of the invention (Fig.2) is similar to that of Fig.1 with substrate S2 being composed of any substrate material suitable for a recording medium. A metal layer M2 in the form of a thin film is deposited upon the substrate S2 first. Next, a thin film silicon layer is deposited upon the metal M2. In this case, it is preferred to write upon the upper surface of the medium with laser beam B_3 (or alternative radiation other than a laser beam) rather than with a beam B_4 passing through the substrate to heat the metal directly, as with beam B_1 in Fig.1. Another advantage of the structure of Fig.2 is that the silicon layer on the metal layer M2 provides a passivation layer, _per se_, requiring no additional film to protect the metal layer M2, because the substrate protects the lower surface.

In another embodiment of the invention, a multi-layer optical storage medium (Fig.3) has a substrate S3 which may be a recording disk for

8

high density storage. The next layer is a reflective mirror layer MR, which may be of titanium or other metal which is highly reflective and which is sufficiently refractory. Ti has a melting point of $1668^{o}C$ so that it is suitable for use without degradation. Upon mirror layer MR is deposited a dielectric spacer layer SP which is preferably composed of a material, such as SiO_2, which is of an appropriate thickness to maximize the wavelength of the laser beam B_5 which is directed upon a pair of thin films A and B which are respectively a metal layer and a silicon layer. The materials of films A and B are interchangeable, so that the metal may be on top as film A (as in Fig.1) or below as film B (as in Fig.2). In either case, the light which passes through the films A and B is reflected back to heat the upper films so as to increase the efficiency of the laser beam B_5, thereby requiring less energy from beam B_5 to write data at a given point. Again, the place-ment of the silicon as the upper film A should enhance the efficiency of the data recording function.

Films of silicide (a compound of metal and silicon) have been widely studied for their applications in micro-electronic devices as contact materials.

K N Tu and J W Mayer, chapter 10 in "Thin Films - Interdiffusion and Reactions" Ed. by J M Poate, K N Tu and J W Mayer, Wiley-Interscience, New York (1978).

In forming silicide contacts by reacting a deposited metallic film with Si, a large optical contrast between the silicide and the unreacted metallic film has often been observed. C J Kircher, Solid State Electron. 14,507 (1971).

The present invention arises from a study of optical contrasts. For example, Fig.4 shows the dark spot of a Pd_2Si contact 0.025mm in diameter in an etched hole on an oxidized Si wafer surrounded by a much

brighter Pd area. Fig.5 shows differences in reflectivity between
these and a black reference. These suggested that silicide films
could be considered as potential materials for archival optical
storage, provided that the contrast between the silicide and the
metal (or Si) in reflection is large enough for the application.
Other crucial requirements for materials in arhival optical storage
are a long lifetime, over 10 years at room temperature and non-toxicity.
Findings on reflectivity change and stability of silicide films for the
storage application are discussed below.

The difference in optical reflectivity between metallic films and their
silicides formed on Si wavers was measured. Several transition metal
films of thicknesses shown in Table I were prepared by E-beam deposition
in a vacuum chamber of 13.33224×10^{-6} Pa (10^{-7} torr) onto [100] oriented
Si wafers of about 32mm in diameter, as shown in Fig.6. Optical reflect-
ivity (R_o) shown in Table I is the value measured at $\lambda = 643.7$ nm (Kr laser),
with θ the angle of incidence of light upon the film being zero.

These films were then annealed at proper conditions to form silicides,
and reflectivity values were measured again as shown in Table I. As can
be seen, most pairs of a metal and its silicide show a difference in
reflectivity ΔR greater than 30%. The largest difference observed is
that between Pd and Pd_2Si, about 53%. The difference has been found
to vary with the wavelength of light used, and Fig.7 shows variations
in optical reflectivity of films of Pd, Pt, Pd-Pd_2Si and Pt-PtSi pairs
measured on Si wafers as a function of wavelength of light used. In
the wavelength range shown in Fig.7 ΔR between Pd and Pd_2Si shows a
larger change than that between Pt and PtSi.

10

11

TABLE I

OPTICAL REFLECTIVITY OF BULK SILICIDES

Metal*	Thickness (Å)	R_0 (%)	Silicide	R_1 (%)	ΔR (%)
Pd	2000	81	Pd_2Si	28	53
Pt	1300	83	PtSi	44	39
Ta	2000	58.5	$TaSi_2$	32.5	26
Rh	2000	67	RhSi	37	30
V	3000	48.5	VSi_2	30	18.5
Co	500	68	CoSi	47	21

$\lambda = 643.7$ nm

*Metal films on Si wafer

Palladium and Silicon and Platinum and Silicon

Pd_2Si and PtsI are two compounds which have many desirable properties including stability and optical contrast. Pd_2Si and PtSi are both formed when local spots are heated by a laser beam during recording. Fig.1 shows a schematic drawing of a structure in which the readout is done by reflection. A substrate of Si or a thin film of Si is deposited onto a suitable substrate by means of vacuum deposition technique or CVD process. A thin layer of Pd or Pt film is then deposited onto the Si film, where the thickness of Pd and Pt may range from 20 nm to 60 nm (200Å to 600Å).

The percentage of optical reflectivity of these films ranges from 80% for Pd to 84% for Pt at a wavelength of interest, say 640nm (6400Å). The spectra shown in Fig.7 are for films of 100 nm (1000Å) thickness. Digital information is recorded by local heating of spots

with pulsed laser beam by moving the storage film or by scanning the
laser beam by moving the storage film or by scanning the laser beam over
the stationary storage film. The temperature of the local spots may
exceed several hundred degrees Celsius, and this causes the formation
of compounds such as Pd_2Si and PtSi by thermal diffusion or melting.
The percentage of optical reflectivity of these compounds is very low,
typically less than 40%. For example, at the wavelength of interest,
at 640nm (6400Å), the percent of reflectivity is 28% for Pd_2Si and 44%
for PtSi, as shown in Fig.7 and Table I.

TABLE II

PUBLISHED PHYSICAL DATA

Silicides	Formation Temp. ^{o}C	Activation energy of growth, eV	Growth rate	Melting Point ^{o}C
Pd_2Si	100 - 700	1.3 - 1.5	$t^{1/2}$	1330
Pt_2Si	200 - 500	1.1 - 1.6	$t^{1/2}$	1100

t = time

From P.376, Thin Films -- Interdifussion and Reactions, Ed. by Poate, Tu,
and Mayer, John Wiley & Sons (1978).

As to the lifetime of such devices, consider the diffusion of Pd into Si
at room temperature. Taking 1.4 eV as the average activation energy,
the diffusion distance in 10 years turns out to be 0.55nm.

Although not shown in Fig.1, a dielectric thin film in the thickness
range of 100nm (1000Å) may be deposited over the Pd surface as an anti-
reflection coating which may also serve as a passivation layer, to
enhance the corrosion resistance.

Rhodium - Silicon

In an optical storage disk (Fig.3) the active layers A and B may be Rh on Si or Si on Rh and can be deposited on a SiO_2 dielectric spacer layer SP. The thickness of each active layer, typically less than 15nm, is chosen such that there is maximum contrast between the laser written spot and the unreacted background.

When a thin film of rhodium is in contact with a layer of silicon and heated to a temperature higher than 400°C, reaction takes place at the interface that forms RhSi. Below 377°C no reaction was observed to take place (D. J. Coe, E. H. Rhoderick, P. H. Gerzon, and A. W. Ginsley, "Silicide Formation in Rh-Si Schottky barrier diodes", Inst. of Phys. Conf. Ser. 22, p. 74, 1974), and this makes the Rh system more attractive for long-term storage applications.

The active layers A and B (Si+Rh or Rh+Si) are on a Ti mirror (40 to 50 nm thick) separated by an SiO_2 dielectric spacer (90 to 100 nm thick). Information is stored by local heating of spots with a laser beam where heating causes reaction of Rh and Si to form silicides. The difference in optical reflectivity before and after formation of silicide is sufficient to give an adequate contrast ratio for readback. For example, the reflectivity of a Rh film of 200 nm (2000Å) on Si at the wavelength of interest (643.7 nm) is typically 67%, and this reduces to 37% after formation of RhSi by annealing at 500°C for 60 minutes.

The main advantage of this is that it avoids the difficult process of ablating perfectly circular holes as used in conventional low-temperature storage materials such as Te and Te-based alloys.

The element Rh is known to be almost corrosion free, and other optical files fabricated with Rh film (with very high laser energy) are certified to be archival by the National Bureau of Standards in the United States.of America. Rhodium offers resistance to atmospheric corrosion of the disk, thus providing a longer lifetime than metals which are more reactive.

Although a bi-layer structure is shown for the active layer in FIG. 3, any variation in the structure may be used, for example a trilayer structure of Si-Rh-Si can be employed to optimize the optical properties.

The lifetime of media is determined largely by degradation of the film caused by corrosion or interfacial diffusion.

Corrosion

With respect to corrosion, Pt/Si, Rh/Si and Pd/Si films (where the metal is deposited first and the silicon later) are much less easily corroded than conventional storage media such as Te.

Interfacial Diffusion

Room temperature lifetime of these bi-layer film structures has to be estimated by an accelerated test and by extrapolation using the known silicide growth rate in thicker films measured at higher temperatures. In the case of 200nm Rh films on Si wafers, the growth of RhSi around 400°C was observed to be diffusion-controlled with an activation energy of 1.9eV. See the following references. D. J. Coe, E. H. Rhoderick, D. H. Gerzon and A. W. Ginsely, in "Metal-Semiconductor Contacts", Conference Series No. 22, Institute of Physics, London 1974; S. Petersson, R. Anderson, J. Dempsey, W. Hammer, F. d'Heurle and S. Laplaca, J. Appl. Phys. 51,373 (1980). By extrapolating it to room temperature, a diffusion-like kinetic constant of $10^{-31} cm^2$/sec and an estimated growth of RhSi of 1nm in a period of 10 years are expected, which practically means no growth of RhSi. However, to check experimentally if an under estimate had been made for the reaction rate in very thin films used here, an accelerated test was performed by annealing the Si/Rh bi-layer films at 150°C for periods of up to 98 days. Fig.8

14

shows glancing-incidence Seeman-Bohlin x-ray diffraction spectra of a Si (25nm)/Rh (25nm) film as deposited, annealed at 150°C for 49 days and 98 days. The extra reflections in (d) belong to RhSi. The intensity of the reflections in (a) is less than those of (b) and (d) due to shorter counting time. Only after 98 days is some RhSi formation observed; about 30nm of Rh has been transformed to RhSi estimated from the relative intensity change of Rh reflections before and after the annealing. If the reported 1.9eV activation energy is used to estimate the growth of RhSi at 150°C after 98 days, a growth of about 1nm of RhSi is obtained, which is quite close to the value measured. It is concluded that the bi-layer film structure of Si/Rh will be stable at room temperature over 10 years. However, the same measurement showed that the bi-layer structure of Si/Pt will be marginally stable though satisfactory and Si/Pd will transform to Pd_2Si probably in less than 10 years at room temperature.

In summary, it has been demonstrated that bi-layer film structure of Si and transition metals are promising materials for archival optical storage. They show a large reflectivity change before and after silicide formation and some of them, such as Si/Rh, have extremely good stability at room temperature. Furthermore, they are non-toxic.

Although the large ΔR observed is interesting, the thick films used experimentally are not suitable for optical storage application because they require relatively high laser power in writing.

Much thinner bi-layer thin films of Si/metal have been prepared by consecutive deposition on oxidized Si wafers, fused quartz, and photo-resist coated quartz for reflectivity and stability measurements. The bi-layer configuration of Si/metal/substrate of Fig.2 rather than metal/Si/substrate of Fig.1 was selected because of lower reflectivity, lower writing energy, and better surface passivation by the Si. Three near-noble metals, Pd, Pt and Rh were chosen to form the bi-layers' because their silicides are easier to form than those of refractory metals.

15

This will save power during laser writing, yet it is noted that
there is a trade-off in lifetime if the silicide forms very easily.
The thickness of either the Si or the metal in the bi-layer structure
has been varied in order to investigate the effect of interfacial
interference on reflectivity.

For example, FIG. 9 shows reflectivity-wavelength curves for six Si/Rh
films on quartz with 25nm Rh covered by 15, 20, 25, 30, 35 and 40nm Si
films. The reflectivity shows maxima and minima and they vary with
film thickness. It is noted that these curves show a much stronger
dependence of reflectivity on wavelength than those in FIG. 7. After
annealing at 700°C for 30 minutes to form RhSi silicide, the reflectivity-
wavelength curve for the annealed sample Si (25nm)/Rh (25nm) for example,
is shown by the broken line in FIG. 9. Before annealing, the sample
showed a reflectivity minimum at $\lambda \sim 6630$nm. At this wavelength, which
is desirable for writing, a ΔR of about 47% is observed.

Characterization of Optical Storage Materials

Laser beam writing on Pt/Si and Rh/Si bi-layer films shows that thermal
conductivities of substrates carrying the bi-layer films play an im-
portant role in determining power requirements for the write operation.
With an argon laser (50% duty cycle), only 0.5 - 1.0mw is needed to
write 10μm diameter spots with Rh/Si films on 400Å thick Si_3N_4 window
structures; 10 - 20mw is needed for films on glass substrates, and more
than 35mw is needed for films on higher thermal conductivity Si sub-
strates. For comparison, 2-3mw is typically necessary to write on Te
films on glass substrates. Laser written spots on the Pt/Si and Rh/Si
bi-layer films can also be described in terms of their apparent colours
when viewed by back reflection of white light, or in terms of the local
change in reflectivity for monochromatic light, e.g., argon laser
illumination λ =514.nNm found that blue, red, and yellow spots written
on Rh/Si bi-layers, had reflectivity changes of <5% (blue)-37% (red) and
+68% (yellow), in comparison with adjacent unwritten areas. Transmission

electron microscopy and diffraction were used to determine the struct-
ural modifications responsible for the various colour and reflectivity
changes. For Rh/Si films on thin Si_3N_4 windows, blue areas were
associated simply with grain growth of the metallic Rh. More intense
laser illumination produced red areas, associated with solid state
reaction of the Rh and Si films and formation of a fine grain silicide
of undetermined structure and composition. Still higher laser powers
produced yellow areas, with larger crystals of orthorhombic Rh_5Si_3 and
of an unidentified cubic phase (a = 4.72A).

FIG. 9 shows the reflectivity of a bi-layer of FIG. 2 for indicated
thicknesses of Rh and Si. Note that for a wavelength of 600nm of light
from a laser beam or the like the reflectance of Curve B is zero. Note
the contrast with the RhSi compound curve shown in dotted form. Curve
C is for 250A each of Rh and Si and it has a minimum slightly above zero
at about 660nm. The curve in FIG. 10 shows slightly different results
for Rh nominally 250A and Si 250A after annealing at 700°C for 30 minutes.
At the preferred frequency (of a gallium arsenide laser) the difference
in reflectivity is 47%. Just above 7000A the difference in reflectivity
is very large in percentage terms, nearly infinite according to the data
shown.

FIG. 11 shows the curves of reflectivity percent as a function of wave-
length for a thinner 150A thick film of Rh. Thicknesses G, H and J
of Si are comparable to those for curves C, D and E in FIG. 9, and it
can be seen that the minimum of zero at about 780nm of curve H differs
very substantially from the result shown for curve D in FIG. 9. The
percentage contrast is much greater also at 810nm. It can be seen
that at 600nm a red laser can be used with curve B in Fig.9 and curve
G in Fig.11 to achieve extremely large ratios of reflectivity. Thus
optimization will be enhanced by employing curves of this type for the
material used for recording.

17

Fig.12 shows the percentages of reflectivity as a function of Si thickness for the bi-layer of Fig.2 and the silicide of rhodium in the dotted line curve. For these thicknesses, it can be seen that the maximum difference in reflectivity is provided at 150Å, for an 800nm laser beam. These thicknesses correspond to those for curve A in Fig.9, but no such data is shown in Fig.11.

Fig.13 is of a photograph magnified 30k times of a bright field transmission electron micrograph (TEM) of a mark made by a 5600 Argstrom wavelength laser beam on a cobalt/silicon bi-layer as in Fig.2.

Fig.14 is of a photograph also magnified 30k times of the same mark in the dark field mode. In the centre (dark in Fig.13) is a thinner layer of amorphous Co_xSi_y which has been heated more by the laser beam than the surrounding area. The next oval ring (lighter in Fig.12) is composed of Co_xSi_y amorphous material which is thicker. The dark ring about the light ring in Fig.12 is composed of crystalline CoSi compound material. The surrounding grey area is the bi-layer of Co/Si which is in its unexposed state. The optical contrast of the inner oval with the surrounding area is quite sharp as can be seen.

Rhodium forms similar patterns with two amorphous Rh_xSi_y inner portions. The thinned amorphous centre surrounded by a thicker rim is caused by writing with a level of laser power exceeding the optimum value. This pattern indicates the beginning of formation of a hole in the amorphous centre, where material has been driven away towards the rim. Slightly lower levels of power of the laser beam does not lead to a thickened rim around the amorphous centre.

Fig.15 is of a TEM magnified 20k times which shows three marks made by the same laser on a bi-layer of Au/Si in accordance with Fig.2 where the ratio of Au to Si is 84 atomic percent in the Au/Si Bi-layer according to a microprobe analysis. The centre of the mark is black

where the amorphous material is located. Around the amorphous
material is a ring of crystalline material.

In the TEM photograph magnified 30k times of Fig.16, the bi-layer
is 79 atomic percent silicon and 21 atomic percent gold. The same
laser beam applied to this gold rich material produced a crystalline
mark which has poor characteristics for an optical record because of
the low contrast between the mark and its surroundings. Fig.17 is a
TEM magnified 20k times of a set of marks made in a medium rich in
silicon with 87 atomic percent Si and 13 atomic percent Au. In this
case the centre has been transformed to the amorphous $Au_x Si_y$ material
with the formation of a bubble of material lifted slightly off the
substrate as can be seen by the curvature shading at the lower portion
of the photographs of the TEMs. At the periphery is the crystalline
Au Si compound and then the surrounding material is shown. Application
of a greater period or intensity of laser radiation would cause the
central bubble of amorphous material either to thin out or to collapse
so that the contrast would be better, similarly to the marks in Fig.15.

For optical reflectivity it does not matter whether the mixed bi-layer
in the mark is amorphous or crystalline.

The percentage of optical reflectivity of an Si Au bilayer on an SiO_2
spacer layer on an Al mirror layer on a substrate is shown in Fig.18
for various wavelengths.

Fig.19 shows a Pd/Si chart of reflectivity fraction as a function of
wavelength for a 250A base of Pd coated with six different thicknesses
of Si. For the 8100A GaAs laser, curve N with 300A thickness of Si
will provide the greatest contrast, as can be seen. Curves L and M
have similar minima for lasers in the 5500A and 6700A ranges.

Fig.20 shows a comparison of laser writing with tellurium (Te) and a

19

tFIG. 14 shows a comparison of laser writing with tellurium (Te) and a
Rh/Si bi-layer as a function of power. A power level below 30mw of a
6741Å wavelength laser is required to make a mark on Te. The curve
drops rapidly to below 10% reflectivity at 20mw power. For rhodium/silicon
bi-layers of 300Å each, the reflectivity of the bi-layer is low up to
about 20mw of power and peaks at about 37mw of power reading about 45%.
What happens with a Te coated medium is that the laser begins to open
holes in the Te immediately. With the bi-layer, the first portion of
the curve involves the reflectivity change as Rh and Si mix, and as the
reflectivity curve for Rh/Si declines above 40mw of power, holes open in
the Rh/Si bi-layer. In addition, with Te there is ablation whereas with
the bi-layer of Rh/Si there is no ablation below 30mw, but there is
instead a reaction of the two layers, at least until the power level is
raised high enough to form holes in the material.

Table III shows the writing power required to produce a mark with various
media most of which are thin film bi-layers in accordance with this
invention. Comparison with tellurium is made in the last two entries.
Palladium covered with silicon requires only a short pulse as do Si/Pd
and Rh/Si with the power required being less for Pd/Si, increasing for
Rh/Si and greatest for Si/Pd because of the reflectivity of the metal Pd
being so much higher than Si in the other two cases. With Mo/Si, the
power required to form silicides is only 35mw with a longer pulse of
500ns. For Zr/Si, the power is the same but the pulse length increases
to 800ns and for Nb/Si, the power is less at 30mw but the time of the
pulse required is greater at 1000ns. For Si/Co and Co/Si the power
levels required are low, but the length of the pulse is 1000ns, which
makes the writing speed slow. Au/Ge and Te are included in the table
for the purpose of comparison. The power required to open a hole is
higher and the pulse length is long.

20

TABLE III

COMPARISON OF WRITING POWER
BILAYER STRUCTURE ON GLASS SUBSTRATES

MAT	R(%)	THICK(A)	POWER (mw)		PULSE (ns)
Pd-Si	54	250-500	13* → 64**		100
Si-Pd	72	250-500	70 → 77		100
Rh-Si	7	300-300	28 → 61		100
Si-Co	68	300-300	27 → 68		1000
Co-Si	32	300-300	20 → 52		1000
V-Si	11	300-200	30		1000
Mo-Si	10	300-200	35		500
Zr-Si	15	300-200	35		800
Nb-Si	13	300-200	30		1000
Au-Ge	81	500		82	1000
Te	64	500		16	50
Te	64	500		10	100

*Power required to form silicides.
**Power required to open holes.
Wavelength: 647.1nm.

In summary, Rh/Si provides a high data rate of only 100ns pulse length.
While Te is superior on this basis, requiring lower power or shorter
pulses, it loses in comparison of lifetime. In terms of lifetimes, the
life of Rh is extremely long, Pt is long, Pd less long, and Te extremely
short.

FIG. 20 shows the curves of power required to write on various materials
on different substrates. Except for the Te on PMMA curve, the rest of
the curves are Rh/Si in thicknesses of 300A/300A and 150A/300A. It can
be seen that polyester and PMMA appear to require less energy. The
glass suffers in this comparison from the fact that the thickness of the
Rh was greater.

Clearly, Te requires less power to provide a mark for a given pulse width, and is far more easy to mark than Rh/Si 150Å/300Å on the PMMA substrate. Also, as is obvious, less power is required as the pulse width increases. The slope of the curve seems to be greater for PMMA. For a short pulse width of less than 50ns, the polyester requires a lower power.

Laser Written Spots in Metal/Silicon Bilayer with a Thickness Varying From 300 to 500Å

Single pulse laser writing on Pd/Si, Co/Si and V/Si bi-layer films with a thickness varying from 300 to 500Å, showed that films on AZ resist on glass can be written with 0.88w whereas on glass no effect was observed with less than 1.2w. The N_2 pumped dye laser had a single pulse width of 5ns and was focused to a spot size of about 1μm. Scanning microscopy showed that although at >2.5w holes were blown in the film, intermediate to no effect at <0.8w the film shows shallow mounds in the centre of the spot with one or more concentric grooves towards the edge.

In the cases of Pd/Si and Co/Si, the centre was found to be amorphous but not so in V/Si. All the spots showed silicide formation. No major difference was found in the size of spots with 2 or 10 consecutive pulses into the same area. These results have demonstrated the writing ability of laser on silicide forming films.

TABLE IV

SILICIDE FORMATION BY CONTACT REACTION

ELEMENTS		SILICIDES	
	METAL-RICH SILICIDES	MONO SILICIDES	DISILICIDES
Pt, Pd	Pt$_2$Si 1.3-1.5eV*	PtSi (end phase) 1.6eV*	
Mg	Mg$_2$Si (only phase)		
Ni, Co	Ni$_2$Si 1.5eV	NiSi	NiSi$_2$ (end phase)
Ti,Zr,Hf Fe,Rh,Mn		HfSi RhSi 2.5eV* 1.9eV*	HfSi$_2$
V,Nb,Ta Cr,Mo,W			VSi$_2$ 2.9eV*

*activation energy

Silicide formation is quite systematic. It always starts with metal rich silicides and progresses towards the silicon rich silicides. Near noble metal silicides are easier to form, i.e., form at low temperatures, than silicides of refractory metals. For specific transition metals, Table IV shows the sequence of formation. The lower the activation energy shown, the easier it is to form the silicide.

In the embodiment of the recording medium, according to the invention shown in FIG. 22, the medium 10 comprises a substrate 12 which can be transparent or opaque depending upon the application for which the medium is to be used. A layer 14 of a first material is deposited upon the substrate 12 and this first material is preferably a metal. A layer 16 of a second material is deposited upon the first layer 14, and the second material is preferably a metal or a semiconductor. A passivating layer 18 is deposited upon the medium 10 to protect the materials comprising layers 14 and 16 from corrosion due to exposure to environmental factors during the lifetime of the medium.

Information is recorded in medium 10 by directing an energy beam of suitable power level to the medium. The energy beam is absorbed in layer 16 and, to a lesser extent in layer 14, to cause localized heating in the adjoining areas of layers 14 and 16 of sufficient magnitude to produce a change in the optical properties of the materials comprising layers 14 and 16.

The energy beam, such as beam B1 shown in the drawing, is preferably directed toward the surface 11 of the medium to produce a recorded spot 19. However, should the substrate 12 be transparent to the radiation in the energy beam, beam B2 could as well be utilized to produce recorded spot 19 by directing beam B2 through substrate 12. In this case, the materials comprising layers 14 and 16 would be interchanged.

The exact nature of the change that takes place is not fully understood since the heating takes place in a time which is in the order of 20 nanoseconds. FIG. 25 shows what is believed to occur during recording with localized melting in layers 14 and 16 due to heating by the beam B1 and a mixing of the component materials across their interface as shown by the small arrows. FIGS. 26 and 27 show the recorded area 19 after recording.

Examination of the recorded area 19 with a Scanning Electron Microscope (SEM) shows a flat recorded spot on a flat background, and no noticeable change in composition from inside to outside the recorded spot. The

optical changes are believed to result from either an alloying or
mixture of the two materials comprising layers 14 and 16 or an inversion
of these layers.

Referring to FIG. 23, the configuration of the medium 20 is very similar
to the FIG. 22 embodiment with substrate 22 composed of any substrate
material suitable for a recording medium. Layer 24 is deposited upon
the substrate and this layer is preferably a metal. Layer 26 is
deposited upon layer 24, and layer 26 is preferably a semiconductor.
Note that in this case, a separate passivation layer is not required
since the semiconductor layer 26 also serves as a passivation layer.
Suitable semiconductor materials can be chosen from germanium or
silicon.

The embodiment of the invention shown in FIG. 24 shows a further
configuration of a medium 30 comprising a suitable substrate 32, a first
recording layer 34 which preferably comprises a metal, a second
recording layer 36 which preferably comprises either a metal or a
semiconductor, and a thick passivation layer 38. In this case,
passivation layer 38 can be several thousand Angstroms thick and may
comprise poly(methylmethacrylate) (PMMA) or other suitable polymeric
materials. In this embodiment, the passivation layer 38 is sufficiently
thick so that its surface 40 is not in the same focal plane as the
recording layers 34, 36. This construction has the advantage that minor
amounts of dust or other contaminants on the surface 40 of the medium 30
do not adversely affect either recording or playback operations.

The preferred medium comprises a 200 Angstrom thick layer of Al
deposited on a PMMA substrate, followed by deposition on the Al of a 230
Angstrom thick layer of Ge, and a passivating layer of SiO_2
substantially as shown in FIG. 1. This medium had spots recorded with a
dye laser at a wavelength of 5800 Angstrom, using a pulse width of 10
nanoseconds. No attempt was made to optimize the laser power
requirements, but the tests indicated a power level requirement no
greater than that required for a standard SiO_2 overcoated Te Optical
Recording Material. The recorded spots, when examined by SEM, showed

flat recorded spots along with flat background. The contrast was sufficiently high that reliable reading could be accomplished.

A similar medium was fabricated using a 200 Angstrom thick layer of Al deposited on a PMMA substrate. A layer of Si 350 Angstrom thick was deposited on the Al layer and overcoated with a passivating layer of MgO. The writing energy for a 1000 Angstrom thickness of MgO was slightly higher than that for Ge-Al. The contrast was also less, but the contrast could be varied with the thickness of the MgO layer. The SEM showed a slightly domed spot, but no material was removed, and the reflectivity within the spot was consistently higher than outside the spot.

A medium was made with a 300 Angstrom thickness Pb layer deposited on a PMMA substrate. A 320 Angstrom thick layer of Sn was then deposited over the Pb followed by a 1000 Angstrom thick passivating layer of SiO_2. The writing energy to form a recorded spot was a factor of 2 greater than for the Ge-Al medium. The constrast was also lower than that for other media tested. The SEM shows a segmented effect in the film with individual segments being fully "written" or else completely "unwritten". While the medium was regarded as unsuitable for some applications, it could be used in a digital form of recording.

A medium which may require the lowest laser power comprises a 300 Angstrom thick layer of In deposited on a PMMA substrate, overcoated with a 230 Angstrom thick Ge layer and a passivating layer of SiO_2. Based on the melting point of this combination of materials, the laser power required should be the lowest, however, this has not yet been established by actual tests.

CLAIMS

1. An optical storage medium including first and second adjacent layers (A, B) of different materials which, upon marking with an energy beam, form a marked area having optical properties different from the optical properties of the unmarked areas, said first layer comprising a metal, and said second layer comprising a metal or a semiconductor.

2. A medium according to claim 1, in which the semiconductor is silicon.

3. A medium according to claim 2, in which the metal of the first layer is a transition metal.

4. A medium according to claim 2, in which the metal of the first layer is selected from the group consisting of the group VB, VIB, VIIB and VII elements on the periodic chart, plus Mg and Au.

5. A medium according to claim 2, in which the metal of the first layer is selected from the group consisting of V, Nb, Ta, Cr, Mo, W, Mn, Fe, Co, Rh, Ni, Pd, Pt and Au.

6. A medium according to claim 2, in which the metal of the first layer is selected from the group consisting of Pd, Pt, Cr, Ta, Rh, V and Co.

7.   A medium according to claim 2, in which the metal of the first layer can be locally combined or reacted with silicon by local heating to produce a silicide which is an optically distinguishable mark and which is stable.

8.   A medium according to claim 7, in which the material is not normally combinable or reactable with silicon without local heating.

9.   A medium according to claim 7 or 8, in which the local heating is applicable by laser.

10.   An optical storage medium according to claim 1, in which said metals are selected from the group comprising Al, Au, Pb and Sn and said semiconductors are selected from the group comprising Ge and Si.

11.   An optical storage medium according to claim 1, in which said materials, upon marking with the energy beam, endothermically form the marked area which comprises an alloy or mixture of said materials.

12.   An optical storage medium according to claim 1, in which the material of said first layer is selected from the group comprising Al, Au, Pb, Sn and the material of said second layer is selected from the group comprising Al, Au, Pb, Sn, Ge and Si.

13.   A method of recording data for subsequent optical readout, in which an energy beam is used to apply local heating to first and second adjacent layers, one of which layers is of metal and the other of which

layers is of metal or semiconductor which can be locally combined or reacted with the metal of the first layer by local heating, to produce an optically distinguishable mark and which is stable.

14. A method according to claim 13, in which the metal of the first layer and the metal or semiconductor of the second layer are endothermically reacted or combined together to form the optically distinguishable mark.
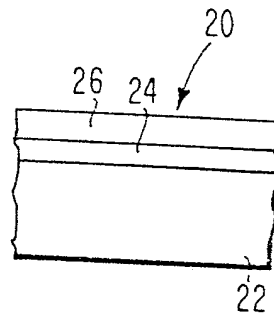
FIG. 1
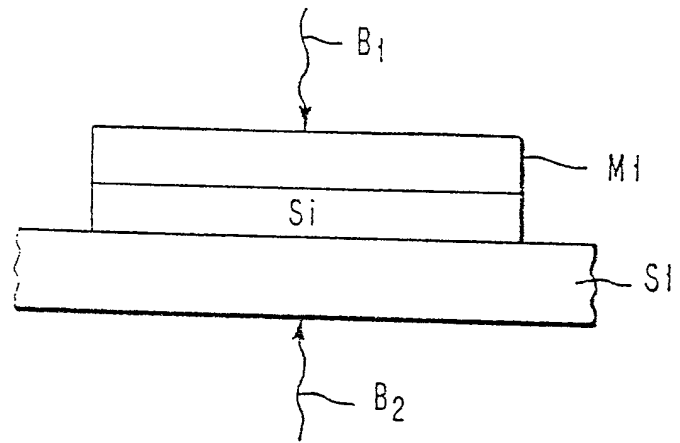
FIG. 2

FIG. 3

FIG. 4

FIG. 5

FIG. 6

θ

| METAL FILM |
| SILICON |
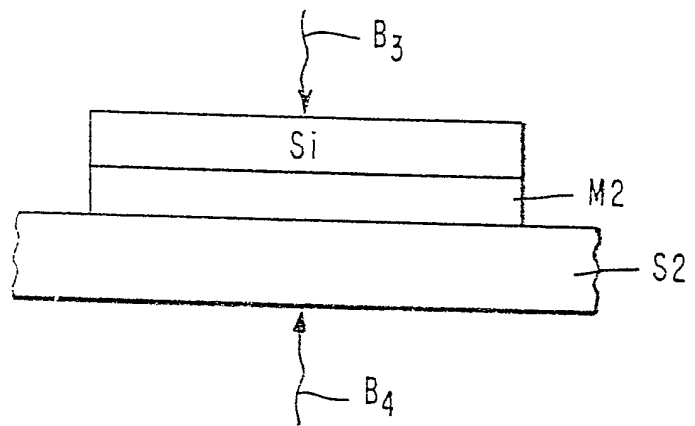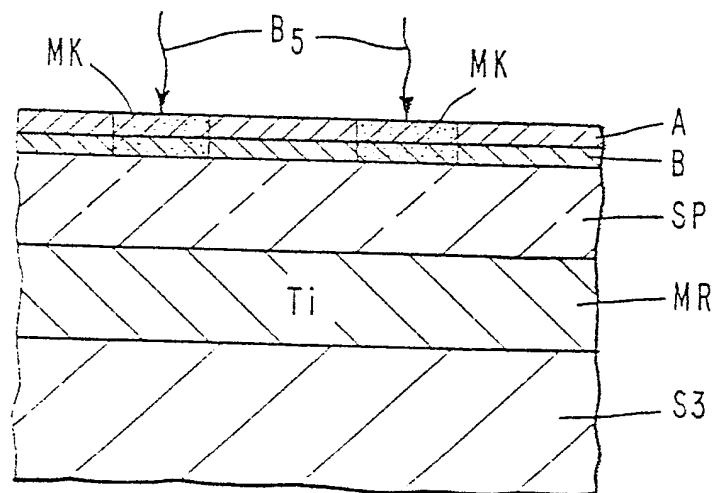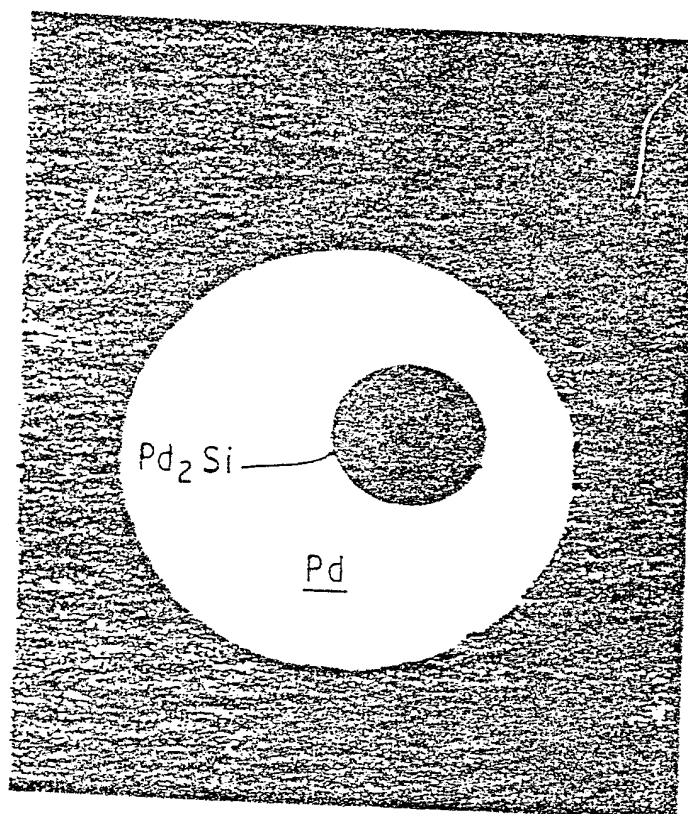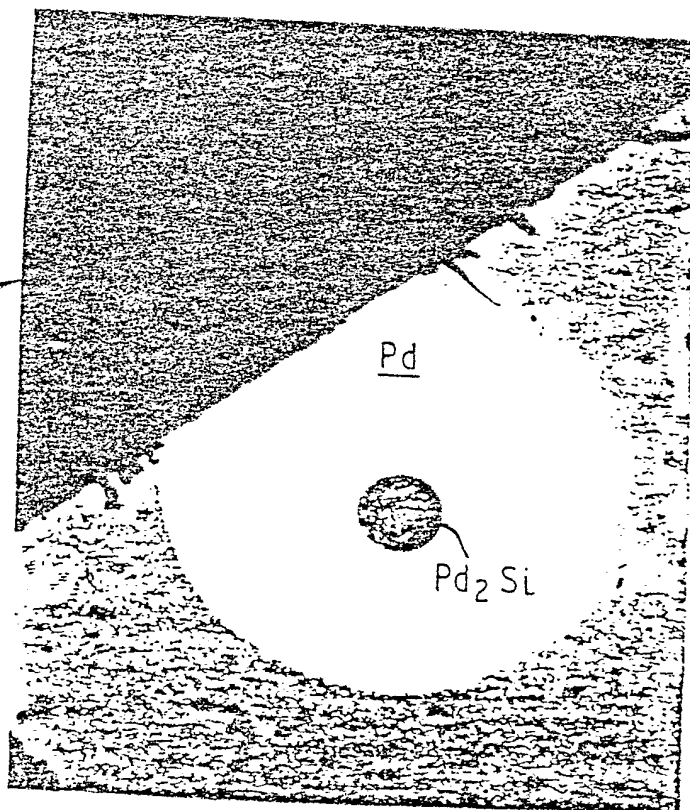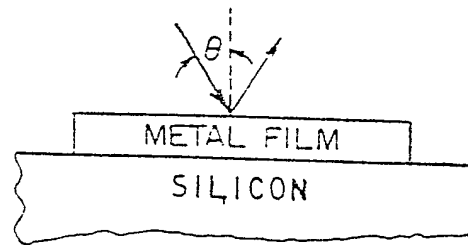
FIG. 7
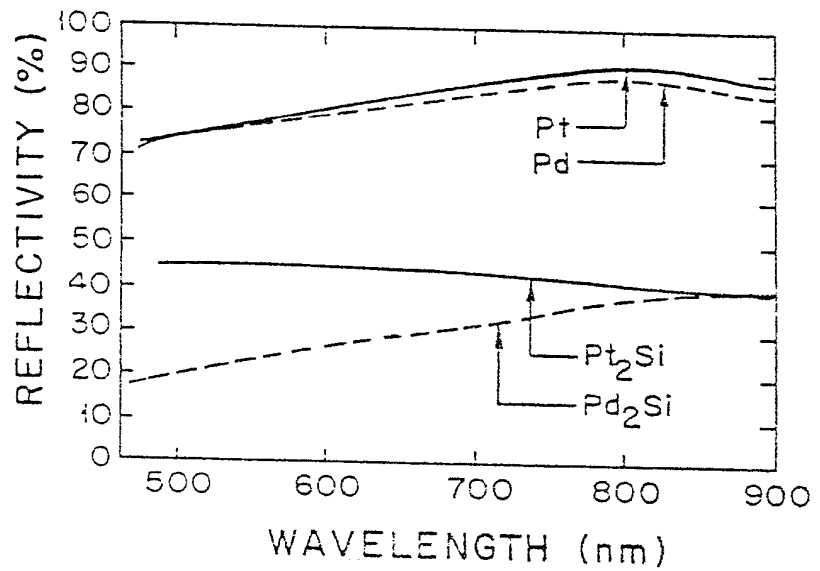
FIG. 18
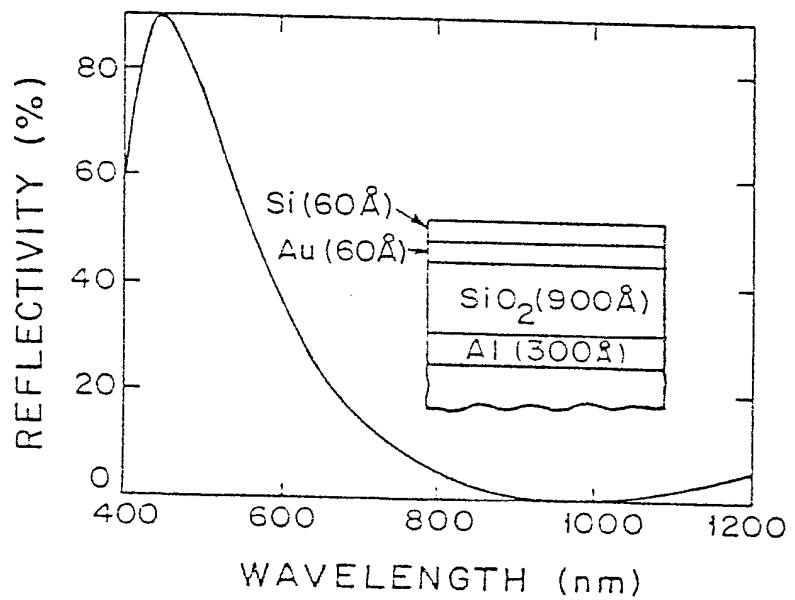
FIG. 8
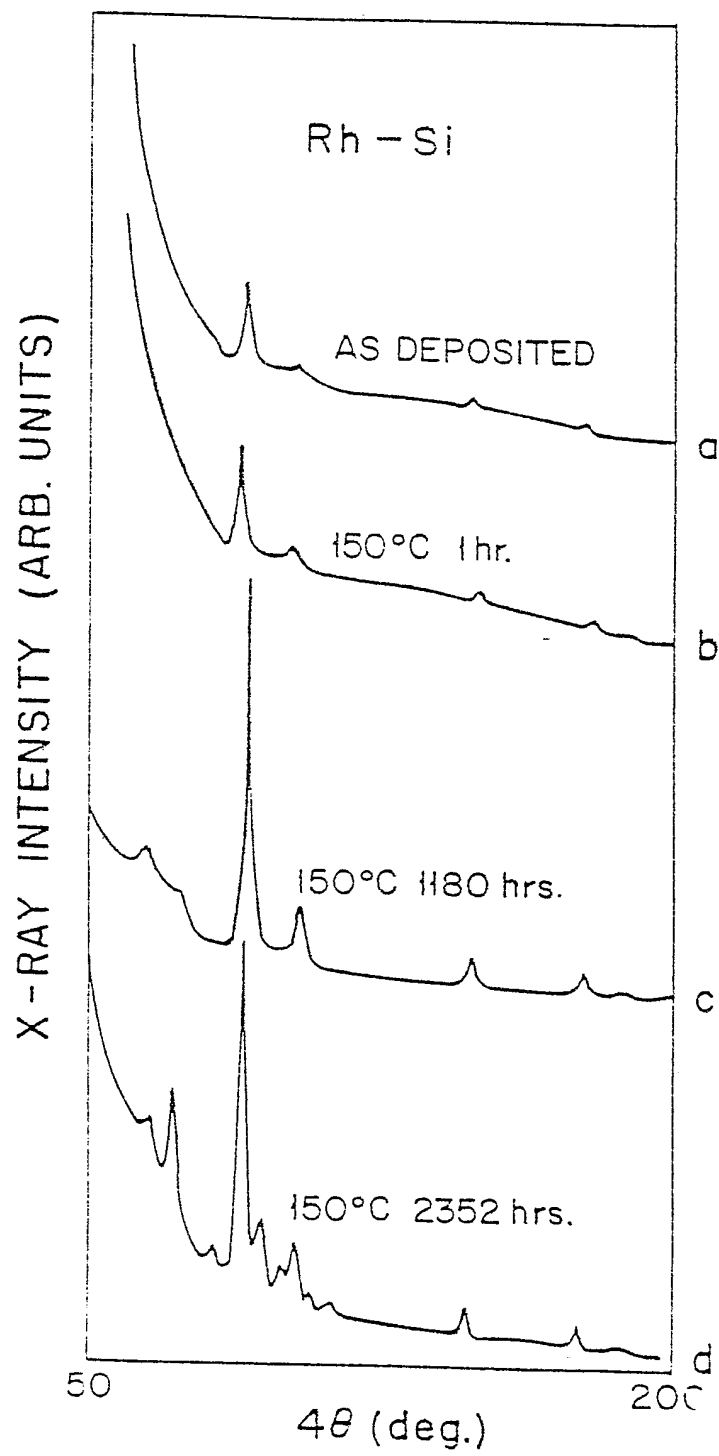
FIG. 9
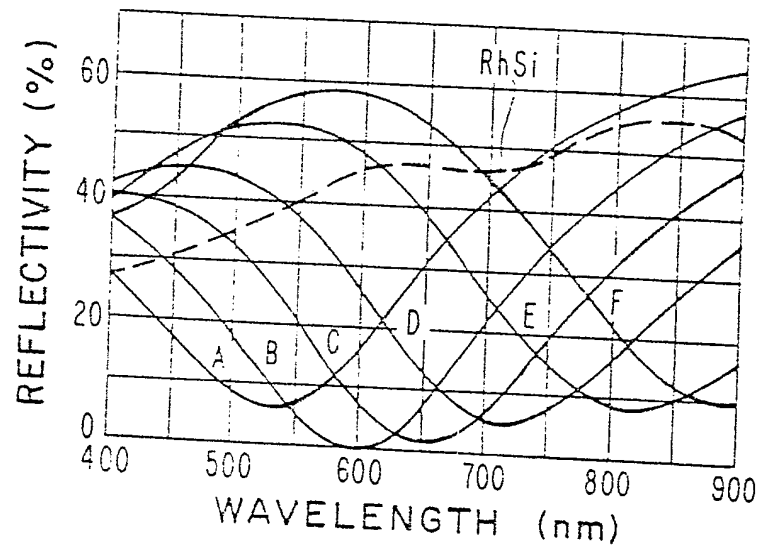
Rh(250A)+Si (150Å)A on Si
        (200Å) B
        (250Å) C
        (300A) D
        (350Å) E
        (400Å) F

FIG. 11

FIG. 19

Si (AS SHOWN)
Pd (250Å)

FIG. 10

Rh (250Å) − Si (250Å)   SiO$_2$/Si

AFTER ANNEAL
700°C 30'

ΔR = 47%

AS DEPOSITED
BILAYER

WAVELENGTH (Å)

FIG. 12

Rh (250 Å) + Si on Si

$\lambda = 800\,nm$
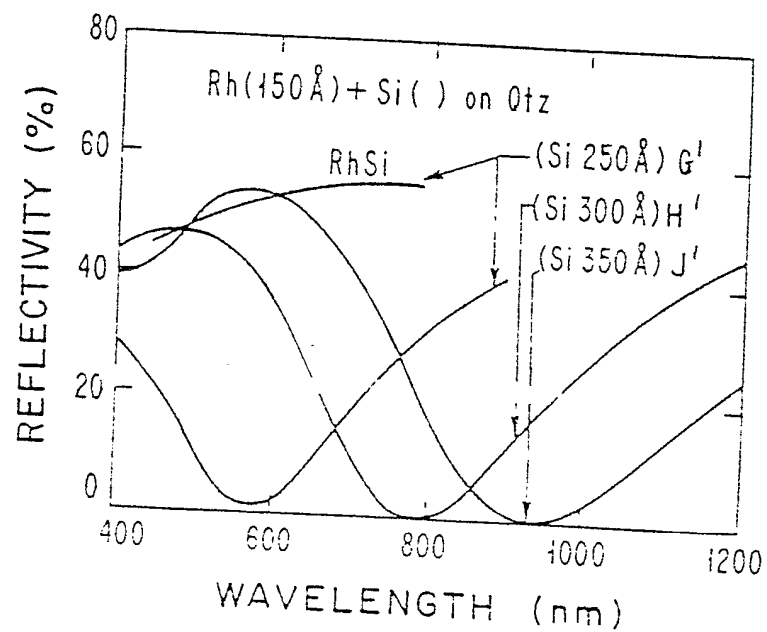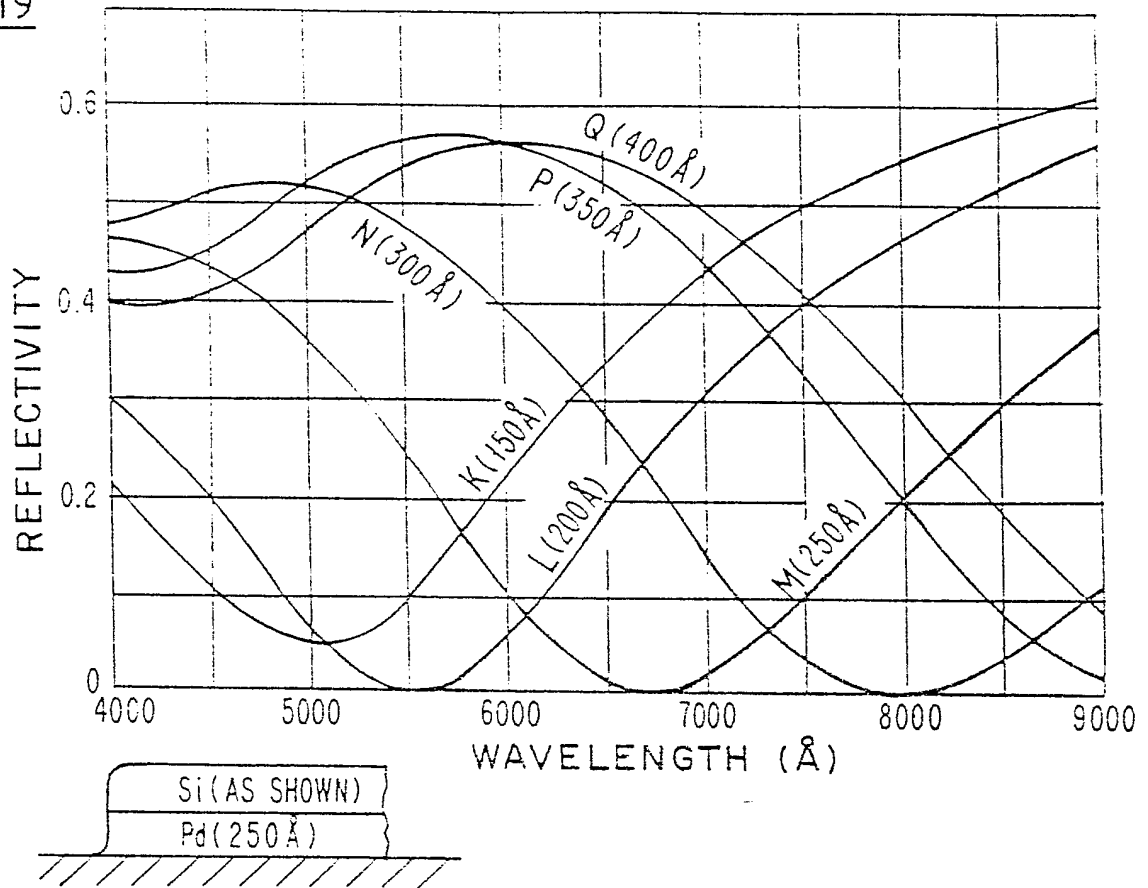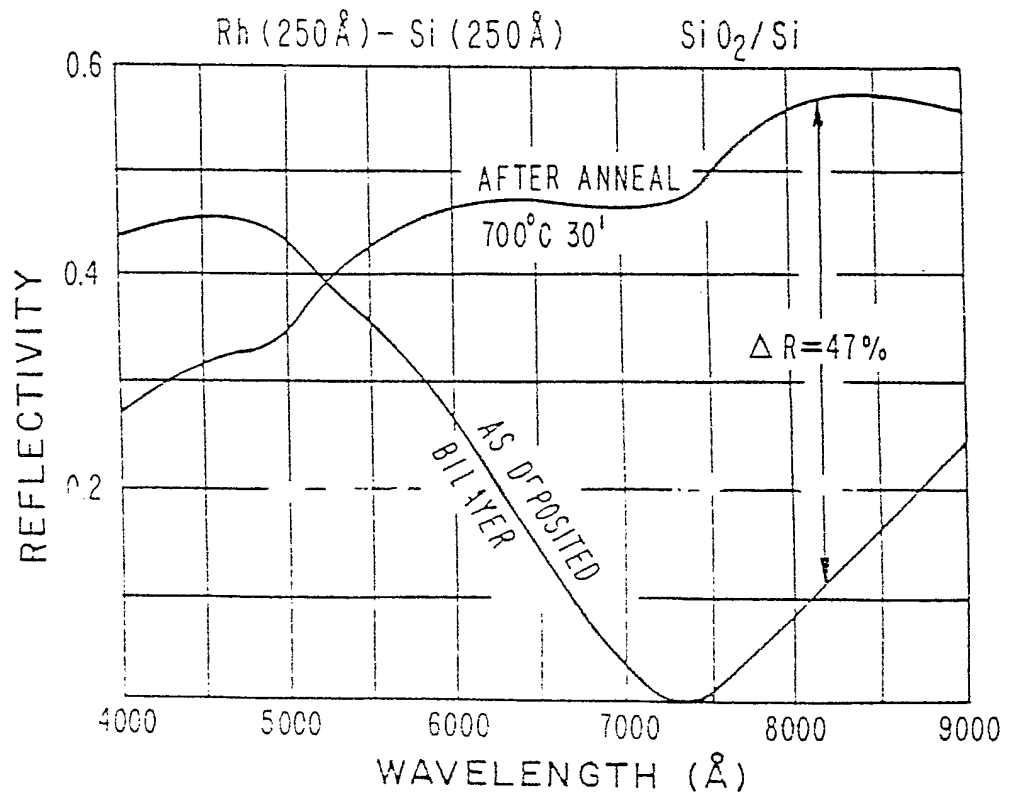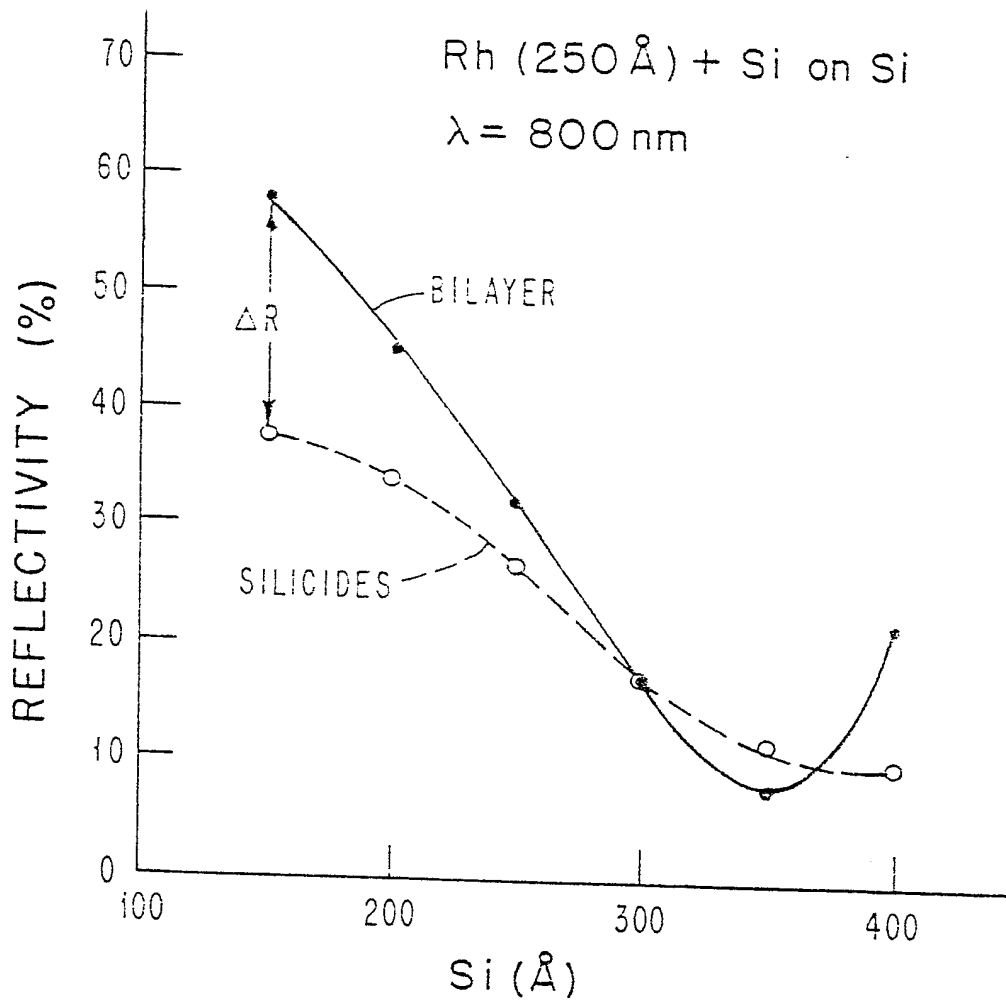
TEM CoSi

FIG. 13

BRIGHTFIELD

1 μ
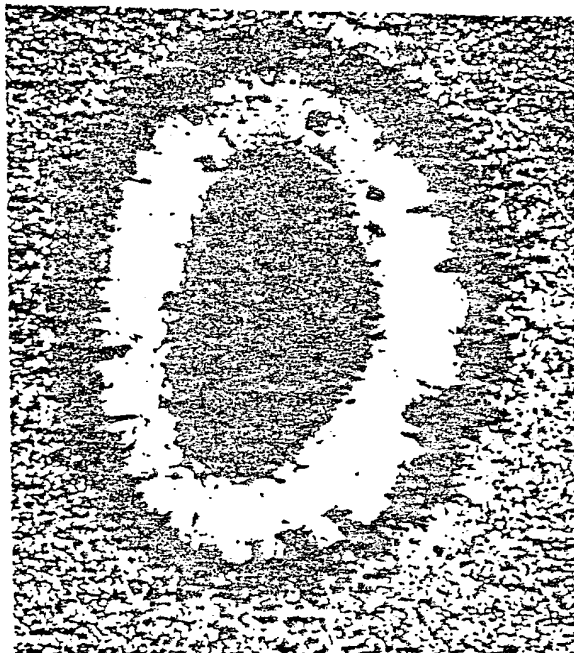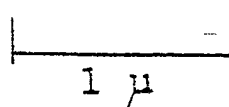
FIG. 14

DARKFIELD

FIG. 15

1 μ
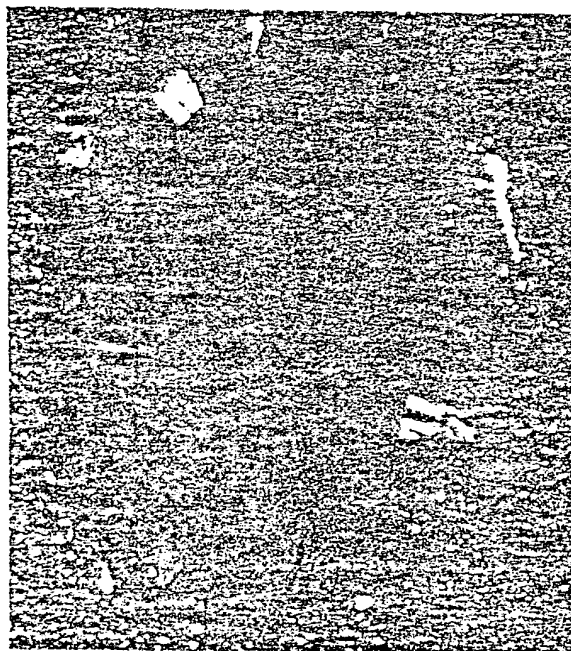
Au - Si (84%)

FIG. 16
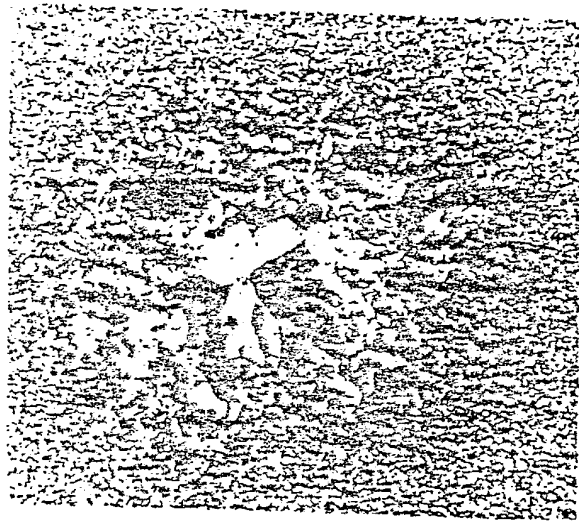
Au - Si (79%)   1 μ

FIG. 17
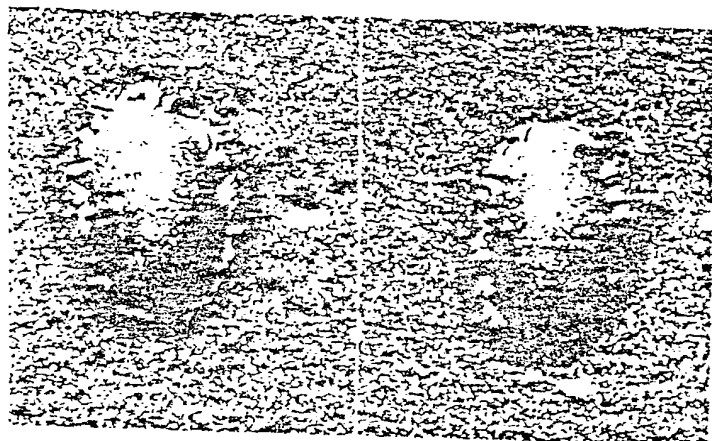
1 μ   Au - Si (87%)

COMPARISON OF LASER WRITING PROCESSES

<u>FIG. 20</u>
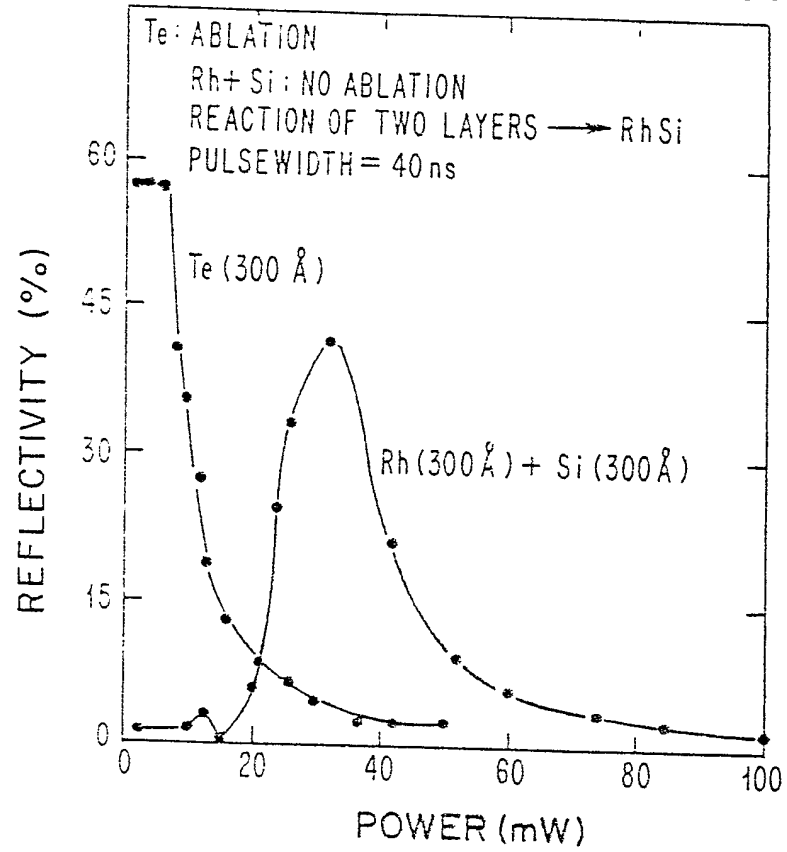
<u>FIG. 21</u>
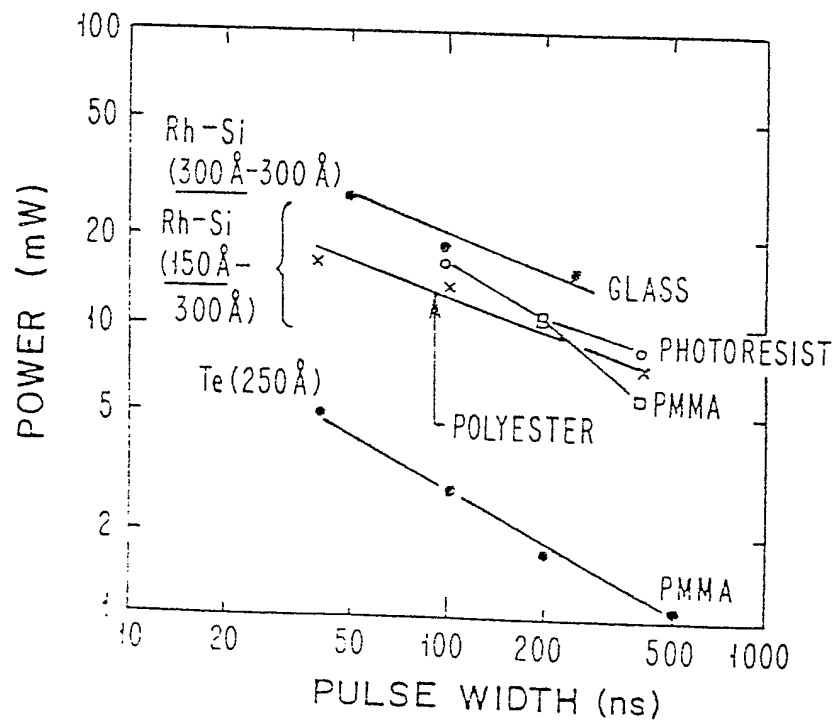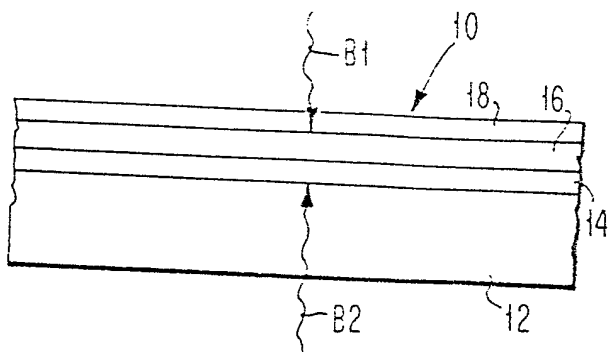
FIG. 22

FIG. 23

FIG. 24

FIG. 25

FIG. 26

FIG. 27